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"CARBON DOPING OF COMPOUND SEMICONDUCTOR EPITAXIAL LAYERS
USING CARBON TETRACHLORIDE"

FINAL REPORT

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November 13, 1989

Submitted to:

U.S Army Research Office
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DAAL03-86-G-0047

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REPORT DOCUMENTATION PAGE

1a. REPORT SECURITY CLASSIFICATION Unclassified		1b. RESTRICTIVE MARKINGS	
2a. SECURITY CLASSIFICATION AUTHORITY		3. DISTRIBUTION/AVAILABILITY OF REPORT Approved for public release; distribution unlimited.	
2b. DECLASSIFICATION/DOWNGRADING SCHEDULE		5. MONITORING ORGANIZATION REPORT NUMBER(S) ARO 23789.2-EL-F	
4. PERFORMING ORGANIZATION REPORT NUMBER(S) DAAL03-86-G-0047		7a. NAME OF MONITORING ORGANIZATION U. S. Army Research Office	
6a. NAME OF PERFORMING ORGANIZATION University of Illinois	6b. OFFICE SYMBOL (if applicable) N/A	7b. ADDRESS (City, State, and ZIP Code) P. O. Box 12211 Research Triangle Park, NC 27709-2211	
8a. NAME OF FUNDING/SPONSORING ORGANIZATION U. S. Army Research Office	8b. OFFICE SYMBOL (if applicable)	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER DAAL03-86-6-0047	
8c. ADDRESS (City, State, and ZIP Code) P. O. Box 12211 Research Triangle Park, NC 27709-2211		10. SOURCE OF FUNDING NUMBERS PROGRAM ELEMENT NO.	TASK NO. PROJECT NO. P-23789-EL-F
11. TITLE (Include Security Classification) Carbon doping of compound semiconductor epitaxial layers using carbon tetrachloride			
12. PERSONAL AUTHOR(S) Brian Cunningham, Gregory Stillman			
13a. TYPE OF REPORT Final	13b. TIME COVERED FROM 8/21/86 TO 8/20/89	14. DATE OF REPORT (Year, Month, Day) 11/13/89	15. PAGE COUNT 5
16. SUPPLEMENTARY NOTATION The view, opinions and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy, or decision, unless so designated by other documentation.			
17. COSATI CODES		18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)	
FIELD	GROUP	SUB-GROUP	
		CCl ₄ , MOCVD, HBT, SIMS, Al _x Ga _{1-x} As, InP	
19. ABSTRACT (Continue on reverse if necessary and identify by block number) A dilute mixture of CCl ₄ in high purity H ₂ has been used as a carbon dopant source for Al _x Ga _{1-x} As grown by low pressure metalorganic chemical vapor deposition (MOCVD). To understand the mechanism for carbon incorporation from CCl ₄ doping, and to provide experimental parameters for the growth of carbon doped device structures, the effect of various crystal growth parameters on CCl ₄ doping have been studied, including growth temperature, growth rate, V/III ratio, Al composition, and CCl ₄ flow rate. Although CCl ₄ is an effective p-type dopant for MOCVD Al _x Ga _{1-x} As, injection of CCl ₄ into the reactor during growth of InP resulted in no change in the carrier concentration or carbon concentration from undoped InP layers. Abrupt, heavy carbon doping spikes in GaAs have been obtained using CCl ₄ without a dopant memory effect. By annealing samples with carbon doping spikes grown within undoped, n-type, and p-type GaAs, the carbon diffusion coefficient in GaAs at 825°C has been estimated and has been found to depend strongly on the GaAs background doping. CCl ₄ doping has been used in the base region of an Npn AlGaAs/GaAs heterojunction			
20. DISTRIBUTION/AVAILABILITY OF ABSTRACT <input checked="" type="checkbox"/> UNCLASSIFIED/UNLIMITED <input type="checkbox"/> SAME AS RPT. <input type="checkbox"/> DTIC USERS		21. ABSTRACT SECURITY CLASSIFICATION Unclassified	
22a. NAME OF RESPONSIBLE INDIVIDUAL Gregory E. Stillman		22b. TELEPHONE (Include Area Code) 217-333-8457	22c. OFFICE SYMBOL

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE

Block 19 continued

bipolar transistor (HBT). HBTs with 3×10^{-4} m self-aligned emitter fingers have been fabricated which exhibit a current gain cutoff frequency of $f_t = 26$ GHz.

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Final Report

Heavily doped p-type layers in GaAs and $\text{Al}_x\text{Ga}_{1-x}\text{As}$ are commonly used in several device structures. They are important in diode lasers and in the base region of heterojunction bipolar transistors (HBTs). Magnesium and Zn are commonly used p-type dopants in metalorganic chemical vapor deposition (MOCVD), but these dopants exhibit problems in obtaining abrupt doping profiles due to the adsorption of these reactants on the internal surfaces of the growth chamber and gas lines. In addition, rapid diffusion of group IIA and IIB elements in GaAs can also lead to dopant redistribution during growth and subsequent processing.

Carbon has been proposed as an alternative dopant to Mg and Zn. Carbon is expected to incorporate only as a shallow acceptor on an As site with very little interstitial incorporation, even at high doping levels. As a result, carbon is expected to have greatly improved diffusion characteristics in comparison to Mg and Zn.

High carbon concentrations have been obtained in GaAs grown by several techniques. High carbon acceptor concentrations have been achieved in GaAs grown by molecular beam epitaxy (MBE) using carbon evaporated from a heated graphite source. Carbon incorporation from trimethylgallium (TMGa), a common Ga growth precursor, has been used to obtain high carbon concentrations in GaAs grown by atomic layer epitaxy (ALE) and metalorganic molecular beam epitaxy (MOMBE).

Several methods for carbon doping have also been proposed for the MOCVD growth technique. Intentional addition of carbon using a number of hydrocarbon sources has not been successful, or has led to films of low carbon content. One researcher has successfully added carbon to GaAs layers with trimethylarsenic. In this work, CCl_4 is used to controllably obtain p-type GaAs and $\text{Al}_x\text{Ga}_{1-x}\text{As}$ with carrier concentrations between $1 \times 10^{16} \text{ cm}^{-3}$ and $1 \times 10^{19} \text{ cm}^{-3}$ in low pressure MOCVD-grown layers. In

addition, CCl₄ doping yields excellent doping abruptness and does not display the memory effects apparent with Mg and Zn doping.

First, a mixture of 500 ppm CCl₄ in H₂ was used to grow heavily doped p-type GaAs by low pressure MOCVD with TMGa and AsH₃ as the group III and V sources, respectively. Carbon acceptor concentrations between $1 \times 10^{16} \text{cm}^{-3}$ and $1 \times 10^{19} \text{cm}^{-3}$ were obtained. In addition, abrupt carbon doping profiles were achieved with no noticeable memory effects. Carrier concentration was studied as a function of CCl₄ flow, V/III ratio, growth temperature, and growth rate using electrochemical capacitance-voltage profiling. Carbon incorporation was found to depend upon CCl₄ flow, V/III ratio, and growth temperature.

Next, to understand the effect of growth parameters on carbon incorporation in CCl₄ doped Al_xGa_{1-x}As, carbon acceptor concentration was studied as a function of Al composition, growth temperature, growth rate, and CCl₄ flow rate using electrochemical capacitance-voltage profiling. The carbon incorporation as a function of Al composition, growth temperature and CCl₄ flow rate was also measured by secondary ion mass spectroscopy (SIMS). All layers were grown by low pressure MOCVD using TMGa and TMAI as group III precursors, and 100% AsH₃ as the group V source. Increased Al composition reduced the dependence of carbon concentration on the growth temperature. Reduced growth rate, which resulted in substantially decreased carbon acceptor concentrations in GaAs, had an insignificant effect on the carrier concentration of Al_{0.4}Ga_{0.6}As. A linear relationship between hole concentration and CCl₄ flow rate in Al_xGa_{1-x}As for $0.0 \leq x \leq 0.8$ was observed. These results indicate that adsorption and desorption of CCl₄ on the Al_xGa_{1-x}As surface during crystal growth plays an important role in the carbon incorporation mechanism.

Intentional carbon doping of low pressure MOCVD grown InP was attempted with a 500 ppm mixture of ¹³CCl₄ in high purity H₂, which was used to obtain carbon acceptor concentrations as high as $1 \times 10^{19} \text{cm}^{-3}$ in GaAs. Under growth conditions similar to

those used for heavy carbon incorporation in GaAs, injection of $^{13}\text{CCl}_4$ into the growth reactor during growth of InP did not produce any measurable change in the carrier concentration of the InP epitaxial layers or any change in the ^{13}C concentration above the ^{13}C background in SIMS analysis. These results support previous low temperature photoluminescence (PL) measurements of high purity InP in which no residual carbon acceptor is observed regardless of the growth technique or conditions, and the hypothesis that carbon is not incorporated in InP grown by any epitaxial technique.

The effects of background doping, surface encapsulation, and arsenic vapor pressure on the diffusion rate of carbon in GaAs were studied by performing anneals on 1000 Å carbon-doped spikes of GaAs grown within 1 µm layers of undoped, Mg doped, and Se doped GaAs. The layers were grown by low pressure MOCVD, and CCl_4 was used as the carbon doping source for the doping spikes. The As_4 vapor pressure during annealing was controlled by the addition of elemental As to the sealed quartz ampoule used for the diffusion. For each As_4 overpressure, two samples, one Si_3N_4 -capped, and one capless were annealed together. All anneals were performed at 825°C for 24 hours. SIMS was used to measure the variation of the carbon concentration as a function of depth for both the as-grown and the annealed samples. The diffusion rate of carbon is found to depend strongly upon the species used for the background doping, being highest in Mg-doped GaAs, and lowest in Se-doped GaAs. The type of surface encapsulation and the As vapor pressure are found to have a very minor effect on the carbon diffusion rate.

Finally, CCl_4 was used as a carbon doping source for the base region of a GaAs/AlGaAs Npn heterojunction bipolar transistor (HBT) grown by low pressure MOCVD. Transistors were fabricated and characterized for dc current gain, emitter-base junction ideality factor, base contact resistance, and external base resistance. Microwave characterization by S-parameter measurement was performed to determine the common emitter current gain and maximum available gain as a function of frequency. Transistors with the base contact area self-aligned to a 3×10 µm emitter finger had a dc current gain

as high as 50, an emitter-base junction ideality factor of $n = 1.2$, and a current gain cutoff frequency of $f_t = 26$ GHz. Transistors of equal emitter area without self-alignment exhibited dc current gain as high as 86, $n = 1.2$, and $f_t = 20$ GHz. A base contact resistance of $R_c = 2.85 \times 10^{-6} \Omega \text{ cm}^2$, and an external base sheet resistance of $R_s = 533.4 \Omega/\text{square}$ were measured. These preliminary results indicate that carbon doping from CCl_4 may be an attractive substitute for Zn or Mg in GaAs/AlGaAs HBT structures grown by MOCVD.